**TABLE 2.1 -- CHARACTERISTIC IONS FOR SEMI-VOLATILE COMPOUNDS[2]**

| Compound | Primary Ion | Secondary Ion(s) | Water MQL[1] µg/L | Solid MQL[1] µg/Kg |
|---|---|---|---|---|
| Napthalene* | 128 | 102, 127 | 0.1 | 6.67 |
| Napthalene-$d_8$ (I.S.)* | 136 | 68 | 1 | 33 |
| Nitrobenzene* | 123 | 77, 65 | 1 | 167 |
| Nitrobenzene-$d_5$ (surr.)* | 82 | 128, 54 | 1 | 33 |
| N-Nitrosodi-n-butylamine | 84 | 57, 116 | 1 | 333 |
| N-Nitrosodiethylamine | 102 | 42, 44 | 1 | 333 |
| N-Nitrosodimethylamine | 42 | 74, 43 | 1 | 167 |
| N-Nitrosodi-n-propylamine* | 70 | 42, 130 | 1 | 33 |
| N-Nitrosodiphenylamine* | 169 | 168, 167 | 1 | 33 |
| N-Nitrosomethylethylamine | 42 | 88, 43 | 5 | 167 |
| N-Nitrosopiperidine | 42 | 114, 55 | 5 | 167 |
| N-Nitrosopyrrolidine | 100 | 41, 42 | 5 | 333 |
| o-Toluidine | 106 | 107, 77 | 5 | 333 |
| p-Dimethylaminoazobenzene | 120 | 77, 225 | 5 | 167 |
| p-Phenylenediamine | 108 | 80, 107 | 50 | 167 |
| Pentachlorobenzene | 250 | 252, 248 | 5 | 667 |
| Pentachloroethane | 167 | 117, 165 | 1 | 33 |
| Pentachloronitrobenzene | 237 | 214, 295 | 5 | 667 |
| Pentachlorophenol* | 266 | 264, 165 | 5 | 33 |
| Perylene-$d_{12}$ (I.S.)* | 264 | 260, 265 | 1 | 33 |
| Phenacetin | 108 | 179, 109 | 5 | 133 |
| Phenanthrene* | 178 | 179, 176 | 0.1 | 6.67 |
| Phenanthrene-$d_{10}$ (I.S.)* | 188 | 94, 80 | 1 | 33 |
| Phenol* | 94 | 65, 66 | 1 | 33 |
| Phenol-$d_6$ (surr.)* | 99 | 42, 71 | 1 | 33 |
| Pyrene* | 202 | 101, 203 | 0.1 | 6.67 |
| Pyridine | 79 | 52, 50 | 10 | 167 |
| Quinoline | 129 | 102, 128 | 5 | 333 |

*Target Compound List  I.S. = Internal Standard  surr. = Surrogate

| TABLE 2.1 -- CHARACTERISTIC IONS FOR SEMI-VOLATILE COMPOUNDS[2] | | | | |
|---|---|---|---|---|
| **Compound** | **Primary Ion** | **Secondary Ion(s)** | **Water MQL[1] µg/L** | **Solid MQL[1] µg/Kg** |
| [1]MQL are periodically evaluated, refer to the LIMS test code for current limits. WI MQL set to 10/3 MDL. | | | | |
| [2]Compound list may be expanded as long as all appropriate demonstration of capability criteria are met. | | | | |

## 3) Definitions

3.1 GC/MS: Gas Chromatograph/Mass Spectrometer

3.2 Organic Free Water: De-ionized (DI) reagent water meeting purity characteristics of ASTM Type II laboratory distilled water (daily conductivity <1.0 umhos/cm).

3.3 Decafluorotriphenylphosphine (DFTPP): Chemical standard used to verify instrument tune parameters.

3.4 Initial calibration verification (ICV): A second source standard utilized to verify the accuracy of the initial calibration.

3.5 Continuing calibration verification (CCV): Calibration standard utilized to verify the accuracy of the established initial calibration.

3.6 Laboratory Control Sample (LCS): An analyte-free matrix spiked with known concentrations of all target analytes. This is used to evaluate and document laboratory method performance.

3.7 Matrix: The component or substrate (e.g., surface water, groundwater, soil) which contains the analyte of interest.

3.8 Matrix Spike (MS): An aliquot of background sample spiked with a known concentrations of all target analytes. The spiking occurs prior to sample preparation and analysis. A matrix spike is used to assess the bias of a method in a given sample matrix.

3.9 Matrix Spike Duplicate (MSD): A duplicate aliquot of the background sample spiked with a known concentrations of all target analytes. Spiking occurs prior to sample preparation and analysis. The MS/MSD pair are used to assess precision and bias of a method in a given sample matrix.

3.10 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

3.11 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

3.12 Sporadic Marginal Exceedance (SME): Statistical probability that a set number of data points will fall outside the normal gaussian distribution curve when evaluated against a multi-component system.

3.13 Extracted Ion Current Profile (EICP): A plot of ion abundance versus time or scan number.

3.14 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of

confidence. The LOQ is also referred to as the method quantitation limit (MQL) or the reporting limit (RL).

3.15 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent.

3.16 Method Detection Limit (MDL) study: the procedure, as described in 40CFR part 136, for determining the LOD based on statistical analysis of 7 low-level replicate spikes.

## 4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HN-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

## 5) Cautions

5.1 Routine preventative maintenance must be performed as scheduled and documented to assure optimum instrument performance. Refer to SOP HN-EQ-004, *Preventative Maintenance* for additional information.

## 6) Interferences

6.1 Organic compounds present in extraction solvents and glassware contamination in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks.

6.2 Raw GC/MS data from all blank samples and spikes must be evaluated for interferences. Determine whether a source of interference is from a sample preparation and/or cleanup step, and perform required corrective action.

6.3 Contamination by carry-over can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an

unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

6.4 Matrix interferences may be caused by contaminants that are co-extracted from a sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

6.5 Benzidine can be subject to oxidative losses during solvent concentration. Care must also be taken to minimize active sites in the chromatographic system.

6.6 Hexachlorocyclopentadiene may be subject to GC thermal decomposition, chemical reaction with acetone, and/or photochemical decomposition.

6.7 N-nitrosodimethylamine is difficult to separate from the solvent front. N-nitrosodiphenylamine may decompose in the inlet system and may elute with diphenylamine

6.8 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic behavior – especially if the chromatographic system is contaminated with high boiling material.

6.9 Pyridine may perform poorly at the method documented GC injection port temperature.

## 7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HN-QS-009).
7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all

method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances
7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

## 8) Sample Collection, Handling, and Preservation

8.1 Water samples are collected in 1-liter glass jars with Teflon-lined lids. Aqueous samples must be extracted within 7 days of collection and stored at 4°C until extraction.

8.2 Soil samples are collected in glass jars with Teflon-lined lids. Solid samples must be extracted within 14 days of sample collection and stored at 4°C until extraction.

8.3 Water samples are prepared by separatory funnel extraction (method 3510C). The samples is first extracted at pH <2 and then extracted at a pH >11.

8.4 Soil samples are extracted by method 3540C (soxhlet extraction), 3541 (automated soxhlet), 3546 (microwave), or 3550 (ultrasonic extraction).

8.5 Sample extracts shall be stored at 0-6 °C in designated areas. Sample extracts must be analyzed within 40 days of the extraction date.

## 9) Equipment and Supplies

9.1 Syringes: 10, 25, 50, 100, 500, 1000, 5000 ul.

9.2 Volumetric Flasks, Class A: 10 ml and 25 ml.

9.3 Analytical Balance: capable of measuring to nearest 0.0001 gram (0.1 milligram).

9.4 Vials-amber glass with teflon-lined screw caps and/or crimp tops.

9.5 Semi-Volatile Unit #1 (SMS4) = HP 6890 Series GC with HP 5973 MSD

9.6 Semi-Volatile Unit #2 (SMS5) = Agilent 6890 GC with Agilent 5973 MSD

9.7 GC Columns – Capable of resolving the compounds listed in Table 2.1 in section 2 of this SOP. Silicone coated fused-silica capillary column - 30 meters long by 0.25 mm ID with a 0.25 µm film thickness.

9.7.1 Restek RTx-5Sil-MS, Catalog # 12623-124.
9.7.2 Zebron Semivolatiles

9.8 Data System: A Windows computer system with Agilent Chemstation is interfaced with a mass spectrometer system to continuously acquire all mass spectra that is generated by the mass spectrometer during the chromatographic run. The data is electronically transferred to EnviroQuant for evaluation and archiving.

9.9 Mass Spectrometer: HP/Agilent system capable of producing a mass spectrum that meets method tune criteria when 50ng of DFTPP (Sec 10.8) is injected.

9.10 HP/Agilent GC/MS Operating Conditions (SMS4 & SMS5): The mass spectrometer is set at 70 electron volts and a scan range of 35-500 m/e. Injection volume = 1 ul.

9.11 GC System Conditions for analysis are listed in table 9.11:

| Table 9.11 - GC System Conditions | | |
|---|---|---|
| System/Condition: | SMS 4 (HP6890/5973) | SMS 5, 6, 7 (Agilent7890/5975) |
| Injector Temperature: | 250°C | 280°C |
| MS Source Temp: | 230°C | 230°C |
| MS Quad Temp: | 150°C | 150°C |
| Transfer line Temp | 280°C | 320°C |
| Helium carrier gas flow program rate: | Mode: Pulsed Splitless<br>Pulse Pressure: 30psi<br>Pulse Time: 1.5 min<br>Split Flow: 52.9 ml/min<br>Split Time: 1.0 min<br>Split Ratio: 54:1<br>Post Pulse Flow: 0.9ml/min | Mode: Pulsed Split<br>Constant Flow: 1.4 min<br>Split Flow: 14 ml/min<br>Split Ratio: 10:1<br>Post Pulse Flow: 0.9ml/min |
| GC Temp Program : | | |
| Initial GC Oven | 40°C, hold 4.0 min. | 40°C, hold 0.5 min. |
| Oven Temp Rate 1: | 200°C @20°C /min. | 260°C @ 40°C /min., hold 0.5 min. |
| Oven Temp Rate 2: | 325°C @25°C /min. | 295°C @ 6°C /min., hold 1 min. |
| Oven Temp Rate 3: | | 325°C @ 25°C/min. |
| Oven Hold Time: | 7 min | 0.22 min |

## 10) Standards and Reagents

10.1 Methylene Chloride - Pesticide grade or higher

10.2 Methanol (MeOH) – Reagent grade or higher

10.3 Stock Acid Surrogates @ 2000 ug/ml: Restek cat. #31025

10.4 Stock BN Surrogates @ 1000 ug/ml: Chem Service BN Surrogate Std Mix, #CLP_2M

**SVOA Surrogates**

| *Surrogate Compound* | *Fraction* |
|---|---|
| | |
| Phenol – $d_6$ | Acid |
| 2-Fluorophenol | Acid |
| 2,4,6-Tribromophenol | Acid |
| Nitrobenzene-$d_5$ | Base – Neutral |
| 2-Fluorobiphenyl | Base – Neutral |
| p-Terphenyl-$d_{14}$ | Base – Neutral |

10.5 BNA Surrogate Mix @ 500 ug/ml

10.5.1 Quantitatively transfer 1000 ul of the stock Acid surrogate mix (Section 10.3) to a clean amber vial

10.5.2 Quantitatively transfer 2000 ul of the stock BN surrogate mix (Section 10.4) to the vial

10.5.3 Quantitatively transfer 1000 ul of methylene chloride to the vial

10.5.4 Label appropriately and store at -10°C

10.5.5 Replace every six months or if degradation is noted.
10.5.6 The expiration date cannot exceed that of any parent mix.

10.6 Stock Internal Standard Mix @ 4000 ug/ml: Restek cat. #31006

10.6.1 Stock SV Internal Standards, 4000 µg/ml: Restek cat. #31006

10.7 Stock Tuning Standard: DFTPP/Pentachlorophenol /Benzidine/4,4'-DDT @ 1000 ug/ml: Restek cat. #31615

10.7.1 Intermediate Tuning Standard @ 50 ug/ml:

10.7.1.1 Add 950 ul of methylene chloride to 50 ul stock standard in a 1 ml vial.
10.7.1.2 This solution must be prepared fresh every 6 months or if degradation is noted. The expiration date of this solution may not exceed that of its parent stock.

10.8 SV Standards: Certified standards are purchased at typical concentrations of 1000 ug/ml to 2000 ug/ml. Stock standards used to prepare calibration intermediates standards are typically prepared from several multi-component mixes that are purchased from a same vender, whose components are vender designed to build larger calibration mixes needed for most 8270 analyte list applications. Should certain calibration compounds co-elute to a point that mass resolutions cannot be adequately made, these compounds shall be separated during preparation and analysis during calibration procedures. The following is a typical example of the Intermediate Calibration Standard

10.8.1 Restek 31850-8270 Mega Mix #1 (1000 ug/mL)
10.8.2 Restek 31852-8270 Benzidines Mix #2 (2000 ug/mL)
10.8.3 Restek 31879 Benzoic Acid Mix #3 (2000 ug/mL)
10.8.4 Restek 31853 1,4-Dioxane Mix #4 (2000 ug/mL)
10.8.5 Absolute Stds 93004 1,2,4,5-Tetrachlorobenzene Mix #5 (2000 ug/mL)
10.8.6 Absolute Stds 19253 OLM 04.2 Add Analytes Mix #6 (2000 ug/mL)
10.8.7 Absolute Stds 70143 2,6-Dichlorophenol Mix #7 (1000 ug/mL)
10.8.8 Accustandard AS-E0183 4-Chlorophenol Mix #8 (5000 ug/mL)

10.9 Typical SV Intermediate Calibration Standard @ 200 ppm:

10.9.1 This type of standard will cover the routine Target Analyte List noted in Table 2.1. Class A volumetric flasks must be used for volume measurements. Standards should be prepared in methylene chloride. Prepare a new intermediate standard every six months.

| Table 10.9 - SV Intermediate Calib. Standard @ 200 ppm | | | | |
|---|---|---|---|---|
| Stock Name | Stock Conc., ppm | Amt Added, ml | Final Volume, ml | Final Conc. ppm |
| Mix 1 | 1000 | 2.0 | 10 | 200 |
| Mix 2 | 2000 | 1.0 | | |
| Mix 3 | 2000 | 1.0 | | |
| Mix 4 | 2000 | 1.0 | | |
| Mix 5 | 2000 | 1.0 | | |
| Mix 6 | 2000 | 1.0 | | |
| Mix 7 | 1000 | 2.0 | | |
| Mix 8 | 5000 | 0.4 | | |

10.10 Initial and Continuing Working Calibration Standards: These standards are prepared at minimally six levels as follows using the intermediate standard prepared in Table 10.9.

| Standard Name | Intermediate Std. @ ug/ml | Amt ul | Final Volume ml | Final Conc. ug/ml | BNA Surrogate ul | Internal Standard ul |
|---|---|---|---|---|---|---|
| Cal A | 200 | 0.5 | 1.0 | 0.10 | 0.5 | 10 |
| Cal B | 200 | 2.5 | 1.0 | 0.50 | 1 | 10 |
| Cal C | 200 | 5 | 1.0 | 1.0 | 2 | 10 |
| Cal D | 200 | 25 | 1.0 | 5.0 | 10 | 10 |
| Cal E | 200 | 50 | 1.0 | 10.0 | 20 | 10 |
| Cal F | 200 | 100 | 1.0 | 20.0 | 40 | 10 |
| Cal G | 200 | 200 | 1.0 | 40.0 | 80 | 10 |
| Cal H | 200 | 250 | 1.0 | 50.0 | 100 | 10 |
| Cal I | 200 | 300 | 1.0 | 60.0 | 120 | 10 |

10.11 LCS Spike Stock Standards: Stock SV Analyte certified standards are purchased at typical concentrations of 1000 µg/ml to 2000 µg/ml. The following is a typical example for the preparation of the LCS Full List Intermediate Spike Standard

10.11.1 8270 Mega Mix Restek cat. #31850.

10.11.2 LCS Spike Working Solution

10.11.2.1 LCS Spike Working Solution @ 40 ug/ml

10.11.2.1.1 Add 1 ml of the Mega Mix Stock (Section 10.11.1) to approximately 30 ml of 1:1 P&T methanol and methylene chloride in a 50 ml Class A volumetric flask.

10.11.2.1.2 Bring to volume with 1:1 P&T methanol and methylene chloride.

10.11.2.1.3 Transfer to an appropriately labeled container.

10.11.2.1.4 Replace every 6 months or if degradation is noted. The expiration date may not exceed that of its parent stock.

10.11.3 Initial Calibration Verification (ICV) Standard: A second source standard must be used to verify the accuracy of the initial calibration curve. The following is a typical example of the ICV standard.

10.11.3.1 ICV Stock Standards @ 2000 ug/ml and 1000 ug/ml

10.11.3.1.1 Benzidine Mixture US-105N Ultra @ 2000 ug/ml in methanol.
10.11.3.1.2 Custom Mix 20927270 Supelco @ 2000 ug/ml in methanol.
10.11.3.1.3 CLP semivolatiles calibration mix Supelco @ 1000 ug/ml in 75:25 methylene chloride and benzene.

10.11.3.2 ICV Working Standard @ 200 ug/ml

10.11.3.2.1 Add 1 ml of 10.11.3.1.1 and 10.11.3.1.2, and 2 ml of 10.11.3.1.3 stock standards to a 10ml Class A volumetric flask.
10.11.3.2.2 Bring to volume with methylene chloride.
10.11.3.2.3 Transfer to an appropriately labeled container.
10.11.3.2.4 Replace every 6 months or if degradation is noted. The expiration date may not exceed that of any of its parent stock.

10.12 Reagent Storage: Transfer the mixtures to multiple 1-mL glass vials with Teflon™-lined caps and store in the freezer at -10 °C. Working standards should be prepared as needed from stocks. Stock standards should be replaced after 1 year or sooner if a manufacturer expiration date has been reached. Prepared intermediate standards should be replaced every 6 months or sooner if a component expires sooner.

10.13 Reagent Preparation Records: Record Stock Standards in the Chemical Inventory Log-book and record all standards prepared in the Standard Preparation Logbook according to SOP HN-QS-001 (latest revision thereof). Label standards appropriately to ensure traceability and to provide for cross-referencing to other records.

10.14 SV Surrogate Spiking Solution @ 100 ug/ml, Environmental Express #M0011 (tinted): This solution contains p-terphenyl-d14, 2-fluorobiphenyl, nitrobenzene-d5, phenol-d5, 2,4,6-tribromphenol, and 2-fluorophenol.

10.15 Storage temperatures

10.15.1 All stock standards should be stored at the manufacturer's temperature recommendations or at -10°C.
10.15.2 All calibration standards and tune standards should be stored at -10°C.
10.15.3 All sample extracts should be stored at 4°C.

## 11) Method Calibration

11.1 Instrument Tune

11.1.1 Inject 50 ng of DFTPP Tuning Mix (Section 10.7.1). The tuning criteria in Table 11.1 must be achieved prior to analytical operations. This criterion must be demonstrated for every twelve-hours of operation.

| Table 11.1 – DFTPP tuning Criteria | |
|---|---|
| Mass | M/z Abundance Criteria |
| 51 | 10-80% of mass 198 |
| 68 | Less than 2% of mass 69 present |
| 69 | 0-100% of mass 198 |
| 70 | Less than 2% of mass 69 present |
| 127 | 10-80 % of mass 198 |
| 197 | Less than 1% of mass 198 |
| 198 | Base peak, 100% relative abundance |
| 199 | 5-9% of mass 198 |
| 275 | 10-60% of mass 198 |
| 365 | Greater than 1 % of mass 198 |
| 441 | Present but less than mass 443 |
| 442 | 50-100% of mass 198 |
| 443 | 15-24 percent of mass 442 |

11.1.2 When performing the above tune, the mass spectrum of DFTPP is acquired using the following approach: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP.

11.1.3 The Tuning Mix also contains pentachlorophenol, benzidine, and DDT. Benzidine and pentachlorophenol are used to evaluate peak tailing. DDT is used to evaluate whether degradation to DDD and DDE is occurring.

11.1.3.1 Tuning standard evaluation for benzidine:

11.1.3.1.1 The calculated benzidine tailing factor should be < 2 and must be < 3.

11.1.3.1.2 Perform column maintenance if the tailing factor does not meet criteria and repeat.

11.1.3.2 Tuning standard evaluation for pentachlorophenol:

11.1.3.2.1 The calculated pentachlorophenol tailing factor should be < 2 and must be < 5.

11.1.3.2.2 Perform column maintenance if the tailing factor does not meet criteria and repeat.

11.1.3.3 Tuning standard evaluation for DDT:

11.1.3.3.1 Degradation of DDT to DDE and DDD should not exceed 20 %.

11.1.3.3.2 Perform column maintenance if the degradation does not meet criteria and repeat.

11.1.3.4 Document instrument tune criteria via a graphics hardcopy of the chromatogram and spectrum, a mass listing normalized to 198 = 100%, and a copy of the tune form.

11.1.3.5 Benzidine, pentachlorophenol, and degradation criteria must be achieved prior to proceeding with analysis.

11.2 Initial Calibration

11.2.1 At a minimum, five calibration solutions (six if quadratic modeling is used) containing both target compounds, surrogates, and internal standards shall be analyzed to document linearity of the instrument. The lowest level of calibration must be at or below the established MRL/PQL, and the highest calibration level must encompass the reported analytical range. The remaining calibrations solutions should be evenly spaced between the lowest and highest standards. Initial calibration must be performed and verified prior to sample analysis. The initial calibration must be completed within 12 hours of the associated instrument tune check (Section 11.1).

11.2.2 Relative response factors (RRF) and percent relative standard deviation (%RSD) for each target compound at each calibration level are tabulated and assessed against method criteria. Refer to Section 15 for calculation of the RRF and the RSD.

11.2.3 System Performance Check Compounds: The compounds listed in Table 11.2.3 are required to meet the minimum average RF values. These checks evaluate compound degradation and system.

Table 11.2.3 – Required RF limits

| *Analyte* | *8270C RF Limits* | *8270D RF Limits* | *Internal Standard* |
|---|---|---|---|
| | | | |
| 1,2,4,5-Tetrachlorobenzene | | 0.010 | Acenaphthene-$d^{10}$ |
| 1,2,4-Trichlorobenzene | | | Napthalene-d8 |
| 1,2-Dichlorobenzene | | | 1,4-Dichlorobenzene-d4 |
| 1,2-Dinitrobenzene | | | Not method defined, default to use closest IS |
| 1,2-Diphenylhydrazine | | | Not method defined, default to use closest IS |
| 1,3-Dichlorobenzene | | | 1,4-Dichlorobenzene-d4 |
| 1,3-Dinitrobenzene | | | Not method defined, default to use closest IS |
| 1,4-Dichlorobenzene | | | 1,4-Dichlorobenzene-d4 |
| 1,4-Dinitrobenzene | | | Not method defined, default to use closest IS |
| 1,4-Naphthoquinone | | | Not method defined, default to use closest IS |
| 1,4-Phenylenediamine | | | Not method defined, default to use closest IS |
| 1-Chloronaphthalene | | | Acenaphthene-$d^{10}$ |
| 1-Napthylamine | | | Acenaphthene-$d^{10}$ |
| 2,3,4,6-Tetrachlorophenol | | 0.010 | Acenaphthene-$d^{10}$ |
| 2,4,5-Trichlorophenol | | 0.200 | Acenaphthene-$d^{10}$ |
| 2,4,6-Trichlorophenol | | 0.200 | Acenaphthene-$d^{10}$ |
| 2,4-Dichlorophenol | | 0.200 | Napthalene-d8 |
| 2,4-Dimethylphenol | | 0.200 | Napthalene-d8 |
| 2,4-Dinitrophenol | | 0.010 | Acenaphthene-$d^{10}$ |
| 2,4-Dinitrotoluene | | 0.200 | Acenaphthene-$d^{10}$ |
| 2,6-Dichlorophenol | | | Napthalene-d8 |

| | | | |
|---|---|---|---|
| 2,6-Dinitrophenol | | | Not method defined, default to use closest IS |
| 2,6-Dinitrotoluene | | 0.200 | Acenaphthene-$d^{10}$ |
| 2-Acetylaminofluorene | | | Not method defined, default to use closest IS |
| 2-Chloronaphthalene | | 0.800 | Acenaphthene-$d^{10}$ |
| 2-Chlorophenol | | 0.800 | 1,4-Dichlorobenzene-d4 |
| 2-Methylnapthalene | | 0.400 | Napthalene-d8 |
| 2-Methylphenol | | 0.700 | 1,4-Dichlorobenzene-d4 |
| 2-Naphthylamine | | | Acenaphthene-$d^{10}$ |
| 2-Nitroaniline | | 0.010 | Acenaphthene-$d^{10}$ |
| 2-Nitrophenol | | 0.100 | Napthalene-d8 |
| 2-Picoline | | | 1,4-Dichlorobenzene-d4 |
| 3,3'-Dichlorobenzidine | | 0.010 | Chrysene-d12 |
| 3,3'-Dimethoxybenzidine | | | Not method defined, default to use closest IS |
| 3,3'-Dimethylbenzidine | | | Not method defined, default to use closest IS |
| 3-Methylphenol | | | Not method defined, default to use closest IS |
| 3-Nitroaniline* | | 0.010 | Acenaphthene-$d^{10}$ |
| 4,6-Dinitro-2-methylphenol | | 0.010 | Phenanthrene-d10 |
| 4-Aminobiphenyl | | | Phenanthrene-d10 |
| 4-Bromophenyl phenyl ether | | 0.100 | Phenanthrene-d10 |
| 4-Chloro-3-methylphenol | | 0.200 | Napthalene-d8 |
| 4-Chloroaniline | | 0.010 | Napthalene-d8 |
| 4-Chlorophenyl phenyl ether | | 0.400 | Acenaphthene-$d^{10}$ |
| 4-Methylphenol | | 0.600 | 1,4-Dichlorobenzene-d4 |
| 4-Nitroaniline | | 0.010 | Acenaphthene-$d^{10}$ |
| 4-Nitrophenol | | 0.010 | Acenaphthene-$d^{10}$ |
| 5-Nitro-o-toluidine | | | Not method defined, default to use closest IS |
| 7,12-Dimethylbenz(a)anthracene | | | Perylene-d12 |
| 2,4-Dinitrophenol | 0.050 | 0.010 | Acenaphthene-$d^{10}$ |
| 4-Nitrophenol | 0.050 | 0.010 | Acenaphthene-$d^{10}$ |
| Acenaphthene | | 0.900 | Acenaphthene-$d^{10}$ |
| Acenaphthylene | | 0.900 | Acenaphthene-$d^{10}$ |
| Acetophenone | | 0.010 | Not method defined, default to use closest IS |
| Aniline | | 0.010 | Not method defined, default to use closest IS |
| Anthracene | | 0.700 | Phenanthrene-d10 |
| Aramite | | 0.010 | Not method defined, default to use closest IS |
| Atrazine | | 0.010 | Not method defined, default to use closest IS |
| Benz(a)anthracene | | 0.800 | Chrysene-d12 |
| Benzaldehyde | | 0.010 | Not method defined, default to use closest IS |
| Benzenethiol | | 0.010 | Not method defined, default to use closest IS |
| Benzidine | | 0.010 | Not method defined, default to use closest IS |
| Benzo(a)pyrene | | 0.700 | Perylene-d12 |
| Benzo(b)fluoranthene | | 0.700 | Perylene-d12 |
| Benzo(e) pyrene | | 0.010 | Not method defined, default to use closest IS |
| Benzo(g,h,I)perylene | | 0.500 | Perylene-d12 |
| Benzo(k)fluoranthene | | 0.700 | Perylene-d12 |
| Benzoic acid | | 0.010 | Not method defined, default to use closest IS |
| Benzyl alcohol | | 0.010 | Not method defined, default to use closest IS |
| Bis(2-chloroethoxy)methane | | 0.300 | Napthalene-d8 |
| Bis(2-chloroethyl)ether | | 0.700 | 1,4-Dichlorobenzene-d4 |
| Bis(2-chloroisopropyl)ether | | 0.010 | 1,4-Dichlorobenzene-d4 |

| | | | |
|---|---|---|---|
| Bis(2-ethylhexyl)phthalate | | 0.010 | Chrysene-d12 |
| Butyl benzyl phthalate | | 0.010 | Chrysene-d12 |
| Caprolactam | | 0.010 | Not method defined, default to use closest IS |
| Carbazole | | 0.010 | Not method defined, default to use closest IS |
| Chlorobenzilate | | 0.010 | Not method defined, default to use closest IS |
| Chlorothalonil | | 0.010 | Not method defined, default to use closest IS |
| Chrysene | | 0.700 | Chrysene-d12 |
| Dacthal | | 0.010 | Not method defined, default to use closest IS |
| Di-n-butyl phthalate | | 0.010 | Phenanthrene-$d_{10}$ |
| Di-n-octyl phthalate | | 0.010 | Perylene-d12 |
| Diallate | | 0.010 | Not method defined, default to use closest IS |
| Dibenz(a,h)acridine | | 0.010 | Not method defined, default to use closest IS |
| Dibenz(a,h)anthracene | | 0.400 | Perylene-d12 |
| Dibenz(a,j)acridine | | 0.010 | Not method defined, default to use closest IS |
| Dibenzofuran | | 0.800 | Acenaphthene-$d^{10}$ |
| Diethyl phthalate | | 0.010 | Acenaphthene-$d^{10}$ |
| Dimethoate | | 0.010 | Not method defined, default to use closest IS |
| Dimethyl phthalate | | 0.010 | Acenaphthene-$d^{10}$ |
| Dinoseb | | 0.010 | Not method defined, default to use closest IS |
| Diphenylamine | | 0.010 | Phenanthrene-$d_{10}$ |
| Diphenyl ether | | 0.010 | Not method defined, default to use closest IS |
| Ethyl parathion | | 0.010 | Not method defined, default to use closest IS |
| Ethyl methacrylate | | 0.010 | Not method defined, default to use closest IS |
| Ethyl methanesulfonate | | 0.010 | Not method defined, default to use closest IS |
| Famphur | | 0.010 | Not method defined, default to use closest IS |
| Fluoranthene | | 0.600 | Phenanthrene-$d_{10}$ |
| Fluorene | | 0.900 | Acenaphthene-$d^{10}$ |
| Hexachlorobenzene | | 0.100 | Phenanthrene-d10 |
| Hexachlorobutadiene | | 0.010 | Napthalene-d8 |
| Hexachlorocyclopentadiene | 0.050 | 0.050 | Acenaphthene-$d^{10}$ |
| Hexachloroethane | | 0.300 | 1,4-Dichlorobenzene-d4 |
| Hexachlorophene | | 0.010 | Not method defined, default to use closest IS |
| Hexachloropropene | | 0.010 | Not method defined, default to use closest IS |
| Indeno(1,2,3-cd)pyrene | | 0.500 | Perylene-d12 |
| Indene | | 0.010 | Not method defined, default to use closest IS |
| Isodrin | | 0.010 | Not method defined, default to use closest IS |
| Isophorone | | 0.400 | Napthalene-d8 |
| Isophthalonitrile | | 0.010 | Not method defined, default to use closest IS |
| Isosafrole | | 0.10 | Not method defined, default to use closest IS |
| Kepone | | 0.010 | Not method defined, default to use closest IS |
| Methapyrilene | | 0.010 | Not method defined, default to use closest IS |
| Methyl methanesulfonate | | 0.010 | Not method defined, default to use closest IS |
| Methyl parathion | | 0.010 | Not method defined, default to use closest IS |
| N-Nitroso-di-n-butylamine | | 0.010 | Not method defined, default to use closest IS |
| N-Nitrosodi-n-propylamine | 0.050 | 0.500 | 1,4-Dichlorobenzene-d4 |
| N-Nitrosodiethylamine | | 0.010 | Not method defined, default to use closest IS |
| N-Nitrosodimethylamine | | 0.010 | 1,4-Dichlorobenzene-d4 |
| N-Nitrosodiphenylamine | | 0.010 | Phenanthrene-d10 |
| N-Nitrosomethylethylamine | | 0.010 | Not method defined, default to use closest IS |

| | | | |
|---|---|---|---|
| N-Nitrosomorpholine | | 0.010 | Not method defined, default to use closest IS |
| N-Nitrosopiperidine | | 0.010 | Not method defined, default to use closest IS |
| N-Nitrosopyrrolidine | | 0.010 | Not method defined, default to use closest IS |
| Naphthalene | | 0.700 | Napthalene-d8 |
| Nitrobenzene | | 0.200 | Napthalene-d8 |
| O,O,O-Triethylphosphorothioate | | 0.010 | Not method defined, default to use closest IS |
| o-Toluidine | | 0.010 | Not method defined, default to use closest IS |
| p-Dimethylaminoazobenzene | | 0.010 | Not method defined, default to use closest IS |
| p-Phenylenediamine | | 0.010 | Not method defined, default to use closest IS |
| Pentachlorobenzene | | 0.010 | Not method defined, default to use closest IS |
| Pentachloroethane | | 0.010 | Not method defined, default to use closest IS |
| Pentachloronitrobenzene | | 0.010 | Not method defined, default to use closest IS |
| Pentachlorophenol | | 0.050 | Phenanthrene-d10 |
| Phenacetin | | 0.010 | Not method defined, default to use closest IS |
| Phenanthrene | | 0.700 | Phenanthrene-d10 |
| Phenol | | 0.800 | 1,4-Dichlorobenzene-d4 |
| Pronamide | | 0.010 | Not method defined, default to use closest IS |
| Pyrazole | | 0.010 | Not method defined, default to use closest IS |
| Pyrene | | 0.600 | Chrysene-d12 |
| Pyridine | | 0.010 | Not method defined, default to use closest IS |
| Quinazoline | | 0.010 | Not method defined, default to use closest IS |
| Quinoline | | 0.010 | Not method defined, default to use closest IS |
| Safrole | | 0.010 | Not method defined, default to use closest IS |
| Sym-Trinitrobenzene | | 0.010 | Not method defined, default to use closest IS |
| Tetraethyldithiopyrophosphate | | 0.010 | Not method defined, default to use closest IS |
| Thionazin | | 0.010 | Not method defined, default to use closest IS |
| Nitrobenzene-$d_5$ (surr.) | | 0.200 | Napthalene-d8 |
| Phenol-$d_6$ (surr.) | | 0.800 | 1,4-Dichlorobenzene-d4 |
| 2,4,6-Tribromophenol (surr.) | | 0.800 | Acenaphthene-$d^{10}$ |
| 2-Fluorobiphenyl (surr.) | | 0.010 | Acenaphthene-$d^{10}$ |
| 2-Fluorophenol (surr.) | | 0.010 | 1,4-Dichlorobenzene-d4 |
| Terphenyl-$d_{14}$ (surr.) | | 0.010 | Chrysene-$d_{12}$ |

11.2.4 Linearity

11.2.4.1 The %RSD from the initial calibration must be ≤ 20% for a target compound if average response factor is to be used.

11.2.4.2 If linear regression or quadratic calibration is used, the correlation coefficient "r" must be > 0.995 or the coefficient of determination "$r^2$" must be > 0.99. The use of quadratic calibration requires six calibration points at a minimum.

11.2.4.3 Upon compounds passing calibration criteria with designated curve options, up to 10% of the compounds may exceed 20% RSD and r > 0.995 or "$r^2$" > 0.99, provided that the %RSD ≤ 30%.

11.2.5 Initial Calibration Verification

11.2.5.1 Upon completion of the initial calibration, the curve must be verified by analysis of a second source calibration standard falling at or near the approximate mid-point of the curve.

11.2.5.2 For Wisconsin specific analytes using a second-order regression, a second, higher level verification must be processed.

11.2.5.3 All analytes must be within 20% of the true value when quantitated against the calibration curve, and the RRFs must meet the criteria listed in Table 11.2.3.

11.3 Retention Time Windows

11.3.1 Retention Time Windows

11.3.1.1 Record the retention time (RT) of each analyte peak.

11.3.1.2 Calculate the mean RT and standard deviation (SD) for each peak.

11.3.1.3 The RT Window for each analyte is defined at ± 3 times the SD around the mean RT.

11.3.1.4 If the SD of the RT is 0, a default value of 0.03 minutes should be used to define the window.

11.3.1.5 For closely eluting peaks, the analyst may narrow the RT window documented in the ChemStation Quant ID file in order to minimize false detects.

11.4 Calibration Verification

11.4.1 A continuing calibration standard at the mid-point of the calibration curve must be analyzed at the beginning of each 12-hour analytical period following the instrument tune check and prior to sample analysis.

11.4.2 The continuing calibration standard should be prepared from the same stock used for the initial calibration curve.

11.4.3 For Wisconsin specific analytes using a second-order regression, a second, higher level verification must be processed.

11.4.4 Acceptance Criteria

11.4.4.1 RFs for the CCV are compared to the average RFs in the initial calibration, and evaluated against the minimum RFs in Table 11.2.3.

11.4.4.2 For each analyte and surrogate using average response factor, the percent difference (%D) between the mean RF as established by the initial calibration and the continuing calibration RF must be ≤ 20%.

11.4.4.3 For analytes using an alternate fit (linear, quadratic), the % drift must be calculated, and must be ≤ 20%.

11.4.4.4 Up to 20% of the compounds in the calibration verification may exceed the 20%, but must be ≤ 40%. This exception does not apply to compounds detected above the MDL in associated samples.

11.4.4.5 Retention times of the internal standards must be within 30 seconds of those in the mid-level standard of the most recent initial calibration.

11.4.4.6 Areas of the internal standards must fall within 50-200% of those established by the mid-level standard of the most recent initial calibration.

11.4.4.7 For analytes using linear regression, the lowest calibration point should be reprocessed against the curve. The recalculated concentration should be within 30% of the true concentration.

11.4.4.8 If any of the above criteria are not meet, corrective action must be taken to improve instrument performance. Analytical results

associated with failed acceptance criteria in Sections 11.1, 11.2, and/or 11.4 may not be reported.

## 12) Sample Preparation/Analysis

12.1 Sample Preparations:

12.1.1 For aqueous samples, refer to SW846-3510C as documented in SOP HN-EXT-001, *Liquid-Liquid Extraction (Separatory Funnel).*

12.1.2 For solid/soil samples, refer to SW846-3540C as documented in SOP HN-EXT-002, *Soxhlet Extraction of Solid Samples*, SW846-3541 as documented in HN-EXT-003, *Automated Soxhlet Extraction, SW846-3546 as documented in HN-EXT-016, Microwave Extraction, or SW846-3550* as documented in HN-EXT-013, *Ultrasonic Extraction.*

12.1.3 Samples extracts shall be stored at 4°C in the designated SVOA refrigerator pending analysis.

12.2 Sample Extract Analysis

12.2.1 Analysis of sample extracts may begin once criteria specified in Section 11 have been achieved.

12.2.2 Internal Standard Addition:

12.2.2.1 Allow sample extracts to warm to room temperature.
12.2.2.2 Add 10 ul of 4000 ug/ml internal standard (see 10.6).

12.2.2.3 Cap the extract vial, and invert the sample vial several times to mix.
12.2.2.4 Proceed with analysis.

12.2.3 When the analysis is complete, verify that the internal standards, surrogates, and compounds of interest are properly identified and quantified, and that the surrogate recoveries are within the acceptable range for the sample type.

12.2.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place.

12.2.4.1 Additional internal standard is added to the diluted extract to maintain the required 40 ug/ml of each internal standard in the extracted volume.

12.2.5 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion.

12.3 Qualitative Analysis (including Tentatively Identified Compounds or TICs)

12.3.1 Comparing the spectrum and retention time of the compound with that of an established standard performs analyte identification.

12.3.1.1 The sample analyte RT must be within $\pm$ 0.06 RRT units of the RT of the current standard analyzed.
12.3.1.2 For mass spectra comparisons, all ions in the standard spectrum at an intensity of >30% (>10% for TICS) relative to the most abundant ion must be present in the sample spectrum.

12.3.1.3 The above qualifying ions must agree within ±20%.

12.3.2 Structural isomers that produce very similar mass specta should be identified as individual isomers if they have sufficiently different retention times. Sufficient resolution is achieved if the height of the valley between the two isomer peaks is less than 50% of the average of the two peak heights.

12.3.3 When requested, a library search will be performed on each sample to identify any components not matched to calibration standard spectra. This search is performed using the Wiley Mass Spectral Library or the ChemStation NIST library. The analyst will report the 10 largest unknown peaks with a correlation of > 80%. The analyst reviewing the library search results makes final determination, and if no adequate match can be determined, the compound is reported as an UNKNOWN.

12.4 Quantitative Analysis:

12.4.1 The internal standard method is used for quantitation of target compounds identified and uses the appropriate ion area for all determinations.

12.4.2 Sample concentrations exceeding the upper calibration limit must be diluted and reanalyzed.

12.4.3 All quantitation must be conducted relative to the current initial calibration.

12.4.4 When target analytes are detected and are affected by co-eluting peaks that interfere with reliable quantitation, the sample extract should be diluted and reanalyzed or alternatively, the reported data shall be flagged as "estimated".

## 13) Troubleshooting

13.1 Refer to Agilent GC-MS hardware manual for specific technical guidance.

## 14) Data Acquisition

14.1 Data is collected with "Chemstation" data acquisition software.

14.2 EnviroQuant data processing software converts the acquired signal information from "Chemstation" into concentration data.

14.3 LIMS receives the processed data in its data entry module and links the data to the samples in a specific work order. The QC batch data is also linked to the data.

## 15) Calculation, and Data Reduction Requirements

15.1 Initial Calibration (ICAL) Calculations (RRF and RSD): Calculate the average relative response factor (Ave. RRF or Ave.RF) for each compound across the five or more calibration concentrations using the below equations:

$$RF = \frac{A_x \, x \, C_{is}}{A_{is} \, x \, C_x}$$

Where:

$A_x$ = Area of the characteristic ion for the compound being measured.
$A_{is}$ = Area of the characteristic ion for the specific internal standard.
$C_{is}$ = Concentration of the specific internal standard.
$C_x$ = Concentration of the compound being measured.

15.2 Percent Relative Standard Deviation (% RSD): Calculate the %RSD(s) for each compound as follows:

$$\%RSD = \frac{SD}{\bar{x}} \, x \, 100$$

Where:

RSD = relative standard deviation.

$\bar{x}$ = mean of Response factors (Rfs).
SD = standard deviation of average Rfs.

15.3 Continuing Calibration

15.3.1 Calculation of % drift (regression model curve fits) by using the following formula:

*% Drift= [(Calculated conc - Theoretical conc) x 100] / Theoretical conc*

15.3.2 Percent difference (response factor calibration fit) is calculated as follows:

$$Percent\ Difference = \frac{\overline{RRf_I} - RRf_C}{\overline{RRf_I}} \, x \, 100$$

$\overline{RRfi}$ = average relative response factor from the initial calibration

$RRF_c$ = response factor from current verification check standard

15.4 Analyte Calculations, aqueous samples:

$$concentration\ (ug/l) = \frac{(A_x)(I_s)(V_t)(d)}{(A_{is})(RRF)(V_o)}$$

Where:

$A_x$ = Area of characteristic ion for compound being measured.
$I_s$ = Amount of internal standard (ug).
$V_t$ = Volume of total extract in ml
$A_{is}$ = Area of the characteristic ion for the specific internal standard.
RRF = Relative Response factor for compound being measured.
$V_o$ = Volume of water extracted in L
d = Dilution factor

15.5 Analyte Calculations, soil or solid waste samples:

$$Concentration\ (ug/kg) = \frac{(A_x)(I_s)(V_t)(d)}{(A_{is})(RRF)(W_s)}$$

$A_x$, $I_s$, $A_{is}$, RRF, $V_t$ and d = same as for water.
$W_s$ = weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

15.5.1 The analyst must know how to use the above equations. The equations are

necessary tools for troubleshooting calibration files, ID files, and acquired data files. The sample concentration is quantified and a report generated utilizing computer software.

15.5.2 The equations used for calculating concentrations of TICs are the same as those used for target compounds with the following modifications: peak areas are derived from the total ion instead of the extracted ion, and a RRF of 1 is assumed. TIC concentrations are always reported as estimated values and have an associated data qualifier reported.

15.6 QC Calculations: LIMS calculates the percent recovery for various QC samples (MS, MSD, LCS) according to the following equations:

15.6.1 Surrogate Recovery: Sample, matrix spike/matrix spike duplicate, duplicate, and blank samples are all spiked with surrogates prior to extraction. The surrogate percent recoveries in these samples should fall into the ranges specified in the method for soil and water samples. If surrogate recoveries fall outside these limits, check for errors in calculations, split peaks, or standard solution degradation. Re-analyze the sample if no apparent problems exist. If the recoveries for the re-analyzed sample are within the ranges, report only the re-analysis. If recoveries are out again, report both analyses.

15.6.1.1 Surrogate percent recovery is calculated as follows:

$$\%R = \frac{(SurrSR)}{SurrSA} \times 100$$

Where:

SurrSR = Surrogate Spiked Sample Result (mg/L or mg/kg).
SurrSA = Surrogate Spike Amount Added (mg/L or mg/kg).

15.6.2 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.6.3 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.6.4 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
$SR_1$ = Sample result for duplicate 1.
$SR_2$ = Sample result for duplicate 2.

## 16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Instrument (DFTPP) Tuning:

16.1.1 Perform at the beginning of each analytical run or every 12 hours whichever comes first.
16.1.2 All criteria specified in Section 11.1 (Table 11.1) must be achieved prior to continued analysis.
16.1.3 If acceptance criteria are not achieved, discontinue operation, perform any necessary instrument maintenance and reanalyze. All samples associated with a failed instrument tune must be reanalyzed after corrective action has been performed.

16.2 Initial Calibration:

16.2.1 A new initial calibration must be generated when CCV criteria are not met, after major instrument maintenance, or after changes in operating conditions.

16.2.1.1 All analytical runs utilized in establishment of the initial calibration curve must clearly document and provide for the traceability of the associated standard used.
16.2.1.2 Upon establishment of a new initial calibration curve, the associated method (w/calibration) must be uniquely identified such that subsequent analyses utilizing the calibration can be clearly identified.

16.2.2 Acceptance Criteria:

16.2.2.1 Initial calibration curve must have 5-points minimally for all analytes; six points are required for second order curve fits.
16.2.2.2 Analytes must meet minimum RF requirements (Table 11.2.3).
16.2.2.3 Target Analytes:

16.2.2.3.1 Target analyte must have a %RSD $\leq$ 15% or,
16.2.2.3.2 Linear regression generates r $\geq$0.995 for analyte or,
16.2.2.3.3 Quadratic regression generates $r^2 \geq$ 0.990.

16.2.3 Corrective Action:

16.2.3.1 Check standard integrity, verify analytical calculations, and perform any necessary instrument maintenance.
16.2.3.2 Repeat the initial calibration sequence.
16.2.3.3 All samples associated with a failed initial calibration must be reanalyzed.

16.2.3.4 Individual data points for a specific analyte may be dropped from the top or the bottom of the curve.
16.2.3.5 A data point may be removed from within the curve as long as it is removed for all of the analytes.

16.3 Initial Calibration Verification (ICV):

16.3.1 Perform an ICV upon completion of each new initial calibration curve.

16.3.1.1 The ICV analysis must clearly document, and provide for the traceability of, the associated standard used.

16.3.2 The ICV must utilize a second source supplier.
16.3.3 The ICV must be at or near the mid-point of the calibration curve.
16.3.4 ICV results must meet accuracy performance criteria within 80-120% of the expected value.
16.3.5 Corrective action:

16.3.5.1 Evaluate standard integrity, verify analytical calculations, and/or perform any needed system maintenance.
16.3.5.2 Repeat the ICV analysis.

16.3.5.3 If the subsequent ICV fails to achieve acceptance criteria, perform a new initial calibration.
16.3.5.4 All samples associated with a failed ICV must be reanalyzed.

16.4 Continuing Calibration Verification (CCV):

16.4.1 The calibration standard must be run prior to sample analysis and every 12 hours thereafter.

16.4.1.1 The CCV analyses must clearly document and provide for the traceability of the associated standard used.

16.4.2 Acceptance Criteria:

16.4.2.1 All analytes must meet minimum RF criteria (Table 11.2.3).
16.4.2.2 All analytes must meet accuracy performance criteria within 80-120% of the expected value.

16.4.3 Corrective Action:

16.4.3.1 Verify standard integrity, verify analytical calculations, and perform any needed instrument maintenance.
16.4.3.2 Repeat the CCV analysis.
16.4.3.3 If the subsequent CCV fails to achieve acceptance criteria, perform a new initial calibration.
16.4.3.4 All samples associated with a failed CCV must be reanalyzed.

16.5 Method Blank:

16.5.1 Analyze a method blank at a frequency of one per analytical batch (per matrix) of 20 or less samples. If the method blank indicates contamination, analyze an instrument blank to demonstrate that the contamination is not a result of

carryover from standards or samples.

16.5.2 Acceptance Criteria: All analytes of interest should be less than ½ the MRL and must be less than MRL.

16.5.2.1 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved quality assurance project plan differs from the above.

16.5.2.2 For Wisconsin compliance samples, the blanks must be evaluated to the MDL.

16.5.2.3 Analytical results associated with blank contamination may be used if analytes of interest are less than 5% of the regulatory limit associated with the analyte or analytes of interest are less than 5% of the sample result for the same analyte, whichever is greater.

16.5.3 Corrective Action:

16.5.3.1 If the method blank fails to achieve acceptance criteria, take corrective action to locate/eliminate the source of the contamination and re-extract/re-analyze all samples associated with the failed blank.

16.5.3.2 If samples cannot be re-run due to insufficient sample or other circumstances, the anomaly must be documented on the associated data checklist and, if applicable, a NCR/CAR submitted to QA per HN-QS-003.

16.5.3.3 Data reported with an associated contaminated method blank must be flagged with a "B".

16.6 Laboratory Control Sample (LCS):

16.6.1 The LCS must be processed with each batch per matrix of 20 samples or less. All samples in the batch must be processed on the same day.

16.6.2 LCS samples shall be spiked with all specified analytes (see Section 21, Attachments).

16.6.3 Acceptance Criteria:

16.6.3.1 Must meet accuracy criteria as outlined in the LIMS test code.

16.6.4 Corrective Action:

16.6.4.1 If the LCS recovery fails to achieve acceptance criteria, the sample batch must be re-extracted and re-analyzed. If reprocessing it is not possible due to lack of sample or expired hold time, reported analytes must be flagged as to probable bias and narrated.

16.7 Matrix Spike and Matrix Spike Duplicate

16.7.1 The MS/MSD pair must be performed at a frequency per batch per matrix of 20 samples or less.

16.7.2 Unless project specified, MS/MSD samples shall be randomly selected and rotated among projects/clients.

16.7.3 MS/MSD samples shall be spiked with all specified analytes (see Section 21, Attachments).

16.7.4 Acceptance Criteria:

16.7.4.1 Must meet accuracy and precision criteria as outlined in the LIMS test code.

16.7.4.2 If the MS/MSD native concentration is greater than four times the spiking level, the acceptance criteria should be considered advisory.

16.7.5 Corrective Action:

16.7.5.1 If MS/MSD recoveries are outside acceptance criteria, the anomaly may be due to matrix effects. Surrogate recoveries and LCS results must be evaluated in order to determine if matrix bias is probable. If associated QC parameters indicate a probable matrix affect, sample results may be reported but must be flagged.

16.7.5.2 If MS/MSD acceptance criteria are not achieved and matrix interference is not apparent (i.e., systemic error), all associated samples must be re-extracted and analyzed. If re-analysis cannot be completed, all results must be qualified accordingly.

16.8 Surrogates

16.8.1 Surrogates must be added to all samples prior to the extraction process and used in the evaluation process.

16.8.2 Acceptance Criteria:

16.8.2.1 Surrogate recovery for interference free matrices and project sample matrices must fall within the following criteria:

16.8.2.2 Must meet accuracy criteria as outlined in the LIMS test code.

16.8.3 Corrective Action:

16.8.3.1 All samples associated with failed surrogate recovery in an interference free matrix must be re-extracted and analyzed. If reanalysis cannot be completed, all associated samples must be flagged as to possible bias and narrated accordingly.

16.8.3.2 All project sample matrices with failed surrogate recovery must be thoroughly reviewed. If recovery failure can be reasonably based upon matrix affects, high dilution, etc, initiate a non-conformance report and flag/report sample results. If no reasonable explanation is present for the failure, re-extract and analyze all associated samples.

16.9 Internal Standards:

16.9.1 Internal standards must be added to all samples prior to analysis.

16.9.2 Acceptance Criteria:

16.9.2.1 The IS retention time widow must be $\pm$ 30 seconds from the associated twelve (12) hour midpoint daily calibration standard

16.9.2.2 The IS areas should not differ from the associated twelve (12) hour midpoint daily calibration standard by more than a factor of two (50 % to 200 %)

16.9.3 Corrective Action:

16.9.3.1 If the internal standards do not achieve acceptance criteria, the sample(s) must be rerun as confirmation of matrix affect. If the rerun does not confirm a matrix effect, review the calculations and check for error. If no errors are found, or if a sample cannot be re-extracted, initiate a non-conformance report flag the sample(s) accordingly, and narrate as to possible bias.

16.9.4 **NOTE:** Several sample types exhibit matrix effects that make recovery of the internal standards and surrogates very difficult. These samples must be run at a dilution to achieve acceptable criteria. However, if target compounds are present in undiluted runs with failing QC (surrogates or internal standards) and are diluted out to achieve passing QC, it may be necessary to report the undiluted analyses with data qualifier flags and an appropriate discussion within the case narrative by project management.

16.10 Deviations and non-conforming events must be documented using a Nonconformance Corrective Action Report (NCAR) or as an Exception Report item on the laboratory review checklist. For mandatory QC failures (e.g. LCS), the NCAR must be submitted to the QA Manager via the NCAR database.

## 17) Data Records Management

17.1 All data is stored both electronically and hard copy for 10 years.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard tracking, analyst must attempt to use one lot of reagents and standards with each batch.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 The effective date of this SOP is the date in the header or last signature date, whichever is most recent.

## 18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

## 19) Method Performance

19.1 Initial Demonstration of Proficiency- Each analyst must perform an initial demonstration of proficiency on a method and matrix basis with a successful analysis of four LCS where acceptable precision and accuracy are generated. The accuracy component must fall within LCS criteria. The precision component must be less than 20% for duplicate RPD data.

19.2 Method Detection Limits (MDLs) must be determined on an annual basis (at minimum) or whenever major modifications are performed.

## 20) Summary of Changes

**Table 20.1 Summary of Changes**

| Revision Number | Effective Date | Document Editor | Description of Changes |
|---|---|---|---|
| R05 | 9/1/12 | CES | Formatting |
| R05 | 9/1/12 | CW | Update Calibration info |
| R06 | 10/15/13 | CES | Formatting; update analyte tables |
| R07 | 9/9/15 | CES | Addition of MCHM/PPH (Appendix B) |
| R08 | 9/15/16 | CES | 10.8.4-10.8.8 added |
| R08 | 9/15/16 | CES | 11.2.5.3 updated to 20% |
| R08 | 9/15/16 | CES | 16.3.4 updated to 80-120% |
| R08 | 9/15/16 | CES | 16.5.2.2 added |

## 21) References and Related Documents

21.1 U.S. Environmental Protection Agency, "SW846-8270D, Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Update IV, February, 2007.

21.2 U.S. Environmental Protection Agency, "SW846-8000C, Determinative Chromatographic Separations", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Update III, June 13, 1997.

21.3 U.S. Environmental Protection Agency, Method 625, 40 CFR Part 136, Appendix A, (current version)

21.4 Dept. of Defense Quality Systems Manual for Environmental Laboratories, Version 3, May 2005

21.5 ALS Environmental Quality Assurance Manual, Revision (most current)

21.6 Appendix A- PNA SIM Analysis

21.7 Appendix B- MCHM/PPH Analysis

# Appendix A

## PNAs by Selective Ion Monitoring (SIM)

(All sections of the 8270 SOP apply unless otherwise specified below)

### Scope and Application

Method 8270 can be used to determine low level Polynuclear Aromatics (PNAs) at a much lower level than a typical scan analysis, by using selective ion monitoring (SIM). Instead of scanning across the entire range of ions, the SIM method only focuses on a few ions so the signal for those ions is much greater. The following compounds may be determined by this method.

| Compound name | | Primary Ion | Secondary Ions | IS Reference |
|---|---|---|---|---|
| Phenol | | 94 | 65,66 | 1,4-Dichlorobenzene-d4 |
| Naphthalene | | 128 | 102,127 | Naphthalene-d8 |
| 2-Methylnaphthalene | | 142 | 141,115 | Naphthalene-d8 |
| Acenaphthylene | | 152 | 151,153 | Acenaphthene-d10 |
| Acenaphthene | | 154 | 153,152 | Acenaphthene-d10 |
| Fluorene | | 166 | 165,167 | Acenaphthene-d10 |
| Phenathrene | | 178 | 176,179 | Phenanthrene-d10 |
| Anthracene | | 178 | 176,179 | Phenanthrene-d10 |
| Fluoranthene | | 202 | 101,203 | Phenanthrene-d10 |
| Pyrene | | 202 | 101,203 | Chrysene-d12 |
| Benzo[a]anthracene | | 228 | 229,113 | Chrysene-d12 |
| Chrysene | | 228 | 226,114 | Chrysene-d12 |
| Benzo[b]fluoranthene | | 252 | 253,125 | Perylene-d12 |
| Benzo[k]fluoranthene | | 252 | 253,125 | Perylene-d12 |
| Benzo[a]pyrene | | 252 | 253,125 | Perylene-d12 |
| Indeno[1,2,3-cd]pyrene | | 276 | 138,277 | Perylene-d12 |
| Dibenzo[a,h]anthracene | | 278 | 139,279 | Perylene-d12 |
| Benzo[g,h,I]perylene | | 276 | 138,277 | Perylene-d12 |
| 1,4-Dichlorobenzene-d4 (IS) | | 152 | 115,150 | NA |
| Phenol-d6(Surr) | | 99 | 71,42 | 1,4-Dichlorobenzene-d4 |
| Naphthalene-d8(IS) | | 138 | 68 | NA |
| Nitrobenzene-d5(S) | | 82 | 128,54 | Naphthalene-d8 |
| Acenaphthene-d10(IS) | | 164 | 162,160 | NA |
| 2-Fluorobiphenyl(S) | | 172 | 171 | Acenaphthene-d10 |
| Phenanthrene-d10(IS) | | 188 | 94,80 | NA |
| 2,4,6-Tribromophenol(S) | | 329 | 331,141 | Phenanthrene-d10 |
| Chrysene-d12(IS) | | 240 | 120,236 | NA |
| 4-Terphenyl-d14(S) | | 244 | 122,212 | Chrysene-d12 |
| Perylene-d12(IS) | | 264 | 260,265 | NA |

Instrument conditions:

**Oven**

Initial temp.: 40$^0$C
Initial time: 4.00 min
Ramps:

| # | Rate | Final temp. | Final time |
|---|---|---|---|
| 1 | 20.00 | 200$^0$C | 0.00 min |
| 2 | 7.00 | 225$^0$C | 5.00 min |
| 3 | 20.00 | 325$^0$C | 2.93 min |

Run time: 28.5 min

**Front inlet**

Mode: Pulsed splitless
Initial temp.: 250$^0$C
Pressure: 7.7 psi
Pulse pressure: 30.0 psi
Pulse time: 1.5 min.
Purge flow: 52.9 mL/min.
Purge time: 1.00 min.
Total flow: 56.4 mL/min.
Gas type: Helium

**Column**

ZB-5 w/Guardian (Phenomenex)
Nominal length: 35.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25um

**SIM parameters**

**Group1**

| Mass | Dwell | Mass | Dwell | Mass | Dwell |
|---|---|---|---|---|---|
| 152 | 50 | 115 | 50 | 150 | 50 |
| 99 | 50 | 71 | 50 | 42 | 50 |
| 94 | 50 | 66 | 50 | 65 | 50 |
| 136 | 50 | 137 | 50 | 108 | 50 |
| 82 | 50 | 128 | 50 | 54 | 50 |
| 102 | 50 | 127 | 50 | 142 | 50 |
| 141 | 50 | | | | |

**Group 2**

| Mass | Dwell | Mass | Dwell | Mass | Dwell |
|---|---|---|---|---|---|
| 164 | 50 | 162 | 50 | 160 | 50 |
| 172 | 50 | 171 | 50 | 170 | 50 |

| | | | | | |
|---|---|---|---|---|---|
| 152 | 50 | 153 | 50 | 151 | 50 |
| 154 | 50 | 166 | 50 | 165 | 50 |
| 167 | 50 | 188 | 50 | 94 | 50 |
| 80 | 50 | 330 | 50 | 332 | 50 |
| 141 | 50 | 178 | 50 | 176 | 50 |
| 179 | 50 | 202 | 50 | 203 | 50 |
| 101 | 50 | 244 | 50 | 122 | 50 |
| 212 | 50 | 142 | 50 | 115 | 50 |

**Group 3**

| Mass | Dwell | Mass | Dwell | Mass | Dwell |
|---|---|---|---|---|---|
| 240 | 50 | 236 | 50 | 102 | 50 |
| 202 | 50 | 203 | 50 | 101 | 50 |
| 244 | 50 | 243 | 50 | 122 | 50 |
| 228 | 50 | 113 | 50 | 229 | 50 |
| 226 | 50 | 114 | 50 | 264 | 50 |
| 260 | 50 | 265 | 50 | 252 | 50 |
| 253 | 50 | 125 | 50 | 276 | 50 |
| 277 | 50 | 138 | 50 | 278 | 50 |
| 279 | 50 | 139 | 50 | | |

**Procedure**

Soil samples are extracted by SW846 method 3540, 3541, 3546, or 3550.
Water samples are extracted by SW846 method 3510.

Surrogate: 100 ug/mL Surrogate Solution (Environmental Express)
50 uL per sample

Spike: 1000ug/mL 8270 MegaMix (Restek)
Working spike: 1mL→ 25 mL 50% Methanol / 50% Methylene chloride
Final concentration: 40ug/mL
LCS/MS/MSD: 50uL each

Post extraction IS: 4000 ug/mL CLP Semi-volatile IS (Absolute Standards)
Working IS: 1 mL → 10mL Methylene chloride
Final Concentration: 400ug/mL
All samples: 10uL each

All QC criteria specified in section 11 must be achieved.

# Appendix B

## Analysis of 4-Methyl-1-cyclohexanemethanol and Propylene glycol phenyl ether by Method 8270

(All sections of the 8270 SOP apply unless otherwise specified below)

### Scope and Application

Method 8270 can be used to determine 4-Methyl-1-cyclohexanemethanol (MCHM) and Propylene glycol phenyl ether (PPH) at a higher level than a typical scan analysis. The following modifications are utilized in the analysis of these compounds.

| Compound name | | Primary Ion | Secondary Ions | IS Reference |
|---|---|---|---|---|
| 4-Methyl-1-cyclohexanemethanol | | 55 | 97, 95 | Naphthalene-d8 |
| Propylene glycol phenyl ether | | 94 | 77, 153 | Naphthalene-d8 |

21.8 SV Standards: Stock standards are prepared at 1000 ug/ml from neat materials.

21.8.1 40 mg of reagent grade MCHM and PPH are brought to a final volume of 40 mL with Methylene Chloride.

21.8.2 Expires 1 year from preparation or if degradation is noted.

21.9 Initial and Continuing Working Calibration Standards: These standards are prepared at minimally six levels as follows using the 1000 ug/mL stock.

| Standard Name | Amt of Stock added ul | Final Volume ml | Final Conc. ug/ml | BNA Surrogate ul | Internal Standard ul |
|---|---|---|---|---|---|
| Cal A | 1 | 1.0 | 1 | 0.4 | 10 |
| Cal B | 5 | 1.0 | 5 | 2 | 10 |
| Cal C | 10 | 1.0 | 10 | 4 | 10 |
| Cal D | 20 | 1.0 | 20 | 8 | 10 |
| Cal E | 50 | 1.0 | 50 | 20 | 10 |
| Cal F | 100 | 1.0 | 100 | 40 | 10 |
| Cal G | 250 | 1.0 | 250 | 100 | 10 |
| Cal H | 500 | 1.0 | 500 | 500 | 10 |

21.10 LCS/MS/MSD Spiking Standard at 1000 ug/ml.

21.10.1 40 mg of reagent grade MCHM and PPH are brought to a final volume of 40 mL with Methylene Chloride.

21.10.2 Expires 6 months from preparation or if degradation is noted.